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Photochromic Solid Films Prepared by Doping with Donor-Acceptor Norbornadienes

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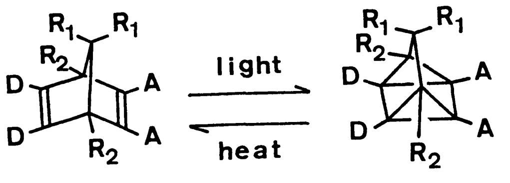
Thin solid films of PMMA doped with donor-acceptor norbornadienes were prepared, and their photochromic properties were examined. The photochromic solid films have absorption at a visible region, and their photochemical decolorization due to valence isomerization proceeded in high quantum yields. They show resistivity for the repeated cycle of the interconversions and no loss in the extinction was observed even after 10^3 times of cycle of reactions.

Compounds having photochromic properties are currently attracting a great interest, *inter alia*, in the fields of the solar energy storage and the photo-image storage.$^{1)}$ Since the formation of cage compounds by intramolecular photocycloaddition is known to bring about the large change in the refractive index,$^{2)}$ this type of reaction might offer us a photochromic system potentially applicable for data storage. The pair of compounds norbornadiene/quadricyclane is a photochromic system, but this system does not have absorption in the region above 300nm and the quantum yield (0.05) of the photo-process is very low. In the course of our study on molecular energy storage for solar energy,$^{3)}$ we have found out that the DA-type substitutional modification of norbornadiene (Eq. 1) provides the molecule having a new absorption in a visible region. Here, the DA-norbornadienes were incorporated in poly(methyl methacrylate) (PMMA) matrix, and the photochromic properties of the resulting solid film based on 1/2 interconversion were examined. The photochromic solid films have some ideal character, i.e., high quantum yields for the photo-process and remarkable resistivity for the repeated cycle of reactions.



1 2 (1)

	D	A	R_1	R_2
a	C_6H_5	CO_2Me	Me	H
b	p-Me-C_6H_4	CO_2Me	Me	H
c	p-MeO-C_6H_4	CO_2Me	Me	H
d	C_6H_5	CN	Me	H
e	p-Me-C_6H_4	CN	Me	H
f	p-MeO-C_6H_4	CN	Me	H
g	C_6H_5	CO_2Me	H	Me
h	C_6H_5	CN	H	Me

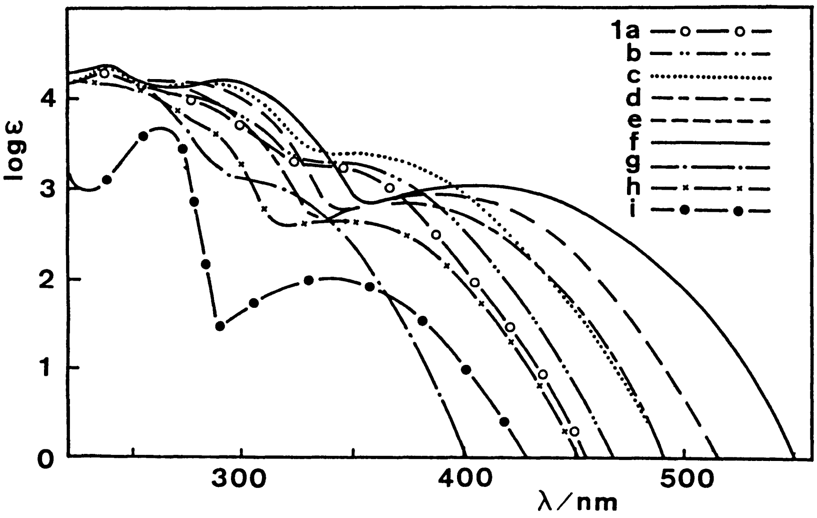


Fig. 1. Absorption spectra of 1a-i in acetonitrile.

Norbornadienes (1a-h) were synthesized by Diels-Alder reaction of appropriate cyclopentadiene derivatives[4)] with dicarbomethoxy- and dicyano-acetylenes. Analytical and spectroscopic data for 1a-h are shown in Table 1.

Fig. 1 shows the CT-absorption bands of 1a-h in a visible region. Especially the absorption cut-off of 1f reaches to 550 nm. Even in the case of 2,3-dicyano-4,5,6-trimethylnorbornadiene (1i),[5)] in which methyl groups were employed as a donor group, the absorption edge comes up to 430 nm.

In a typical run of preparation of the solid film of PMMA incorporating with 1, to a solution of 5 g of PMMA (Wako Pure Chemical LTD., mean value of n = 1200 for $(C_5H_8O_2)_n$) in 25 ml $CHCl_3$ was added a 10 ml solution of 1 of 0.05 M. The resulting solution was sonificated for 1 h to give a homogeneous viscous liquid. The liquid was casted on an optical quartz plate so that a homogeneous thin film

Table 1. Analytical Data of 2,3-Dicarbomethoxy and 2,3-Dicyano-5,6-diarylnorbornadienes

Compd	Mp/°C	Formula	Calcd (Found)/% C	H	N	O	^1H-NMR($CDCl_3$) δ
1a	140	$C_{25}H_{24}O_4$	77.30	6.23		16.47	1.29(s,3H), 1.39(s,3H), 3.79(s,8H),
			(77.26)	(6.13)		(16.18)	7.26(s,10H)
1b	102.5	$C_{27}H_{28}O_4$	77.85	6.78		15.37	1.26(s,3H), 1.35(s,3H), 2.31(s,6H),
			(77.70)	(6.73)		(15.29)	3.75(s,2H), 3.78(s,6H), 7.11(m,8H)
1d	149	$C_{23}H_{18}N_2$	85.68	5.63	8.69		1.21(s,3H), 1.40(s,3H), 3.78(s,2H),
			(85.38)	(5.61)	(8.69)		7.19(s,10H)
1e	132	$C_{25}H_{22}N_2$	85.68	6.33	7.99		1.25(s,3H), 1.43(s,3H), 2.33(s,6H),
			(85.93)	(6.37)	(7.87)		3.80(s,2H), 7.08(s,8H)
1f	127	$C_{25}H_{22}N_2O_2$	78.51	5.80	7.32	8.37	1.24(s,3H), 1.41(s,3H), 3.77(s,2H),
			(78.71)	(5.73)	(7.41)	(8.31)	3.80(s,6H), 6.97(m,8H)
1h	208.5	$C_{23}H_{18}N_2$	85.68	5.63	8.69		1.43(s,6H), 2.41(dd,2H),
			(85.82)	(5.47)	(8.68)		6.98(m,10H)

Table 2. Photochromic Properties of PMMA films doped with 1a-i

System	AE of 1 / nm [a)]	Φ for 1 → 2 [b)]	Thermal reversion of 2 → 1	
			$k \times 10^2$ / min^{-1}	Temp / °C
a	456	0.76	0.608	35
b	469	0.76	1.08	35
c	494	0.55	1.45	35
d	494		5.68	25
e	518		8.83	25
f	551		14.7	25
g	403	0.79	0.116	80
h	454	0.73	0.118	45
i	430	0.79	0.103	81

a) AE is the wavelength of logε=0 in acetonitrile.
b) Excitation wavelength is 334 nm with band path of 10 nm.

was obtained and was dried at ambient temperature in the dark until the constant weight was obtained.

Electronic absorption spectrum of each solid film on quartz plate showed the almost same shape as that of the solution of the respective norbornadiene derivative. Upon irradiation with a xenon lamp complete decolorization of the films was observed. The extinctions were completely recovered by heating the decolorized films. This back process was found to obey the first order kinetics. The rate constants are shown in Table 2. In the case of 1g/2g and 1i/2i systems, no substantial recovery of 1 was observed at room temperature.

Quantum yields for the photochemical conversion of 1 to 2 in the solid films were determined by the modification of the method reported by Saito[6)] according to the equation[7)]

$$\log[(I_n/I_0-1)/(I_n/I_t-1)] = \varepsilon\Phi(1-r/2)I_{ir}t \qquad (2)$$

where t is irradiation time, I_0 and I_t are the transmitted light intensities at t=0 and t=t, I_n is the transmitted light intensity through the film without 1, I_{ir} is the intensity of the incident light, r is the refractance of a sample film and ε is the molar extinction coefficient of 1 at the wavelength of the monochromatic light used. For the determination of the quantum yield according to this principle, a spectrofluorometer (Shimazu RF 502A) was used. The monochromatic excitation light beam was used as incident light for photoreaction. The value I_{ir} was determined by potassium ferioxalate actinometry. Samples were casted on the outer surface of 1 cm x 1 cm quartz cell, which was filled with 10^{-7} M aqueous solution of quinine sulfate. The cell was set in the cell holder so that the excitation light passes through the film, and the transmitted light intensities were determined by monitoring the intensity of fluorescence of the quinine sulfate.[8] Transmitted light intensity was monitored as a function of irradiation time t. The value I_∞ was used as I_n. Using the values thus obtained, plots of the logarithmic value in Eq. 2 vs. irradiation time t gave straight lines through origin, and quantum yields were evaluated from the slope of the plots. As shown in Table 2, the photochemical process in each films proceeded in high quantum yields ranging 0.55-0.8.

Noteworthy is the remarkably high repetitionality of the reactions, photochemical 1 → 2 and thermal 2 → 1. For example, Fig. 2 shows that the chemical oscillations of 1f $\rightleftarrows$ 2f of 10^3 times in solid film proceed without any loss, whereas 20% loss in extinction was observed after the 10^3 cycles of reactions in solution.

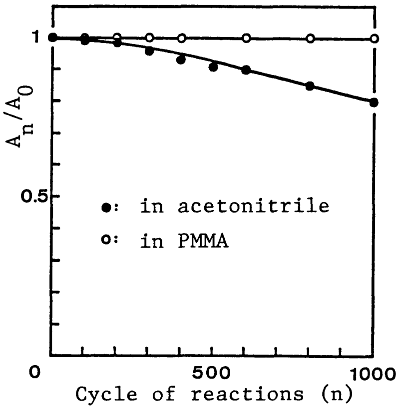


Fig. 2. Repetitionality of 1f/2f system in PMMA and in acetonitrile.

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